

# Fluorinated Graphite Fibers as a New Engineering Material: Promises and Challenges

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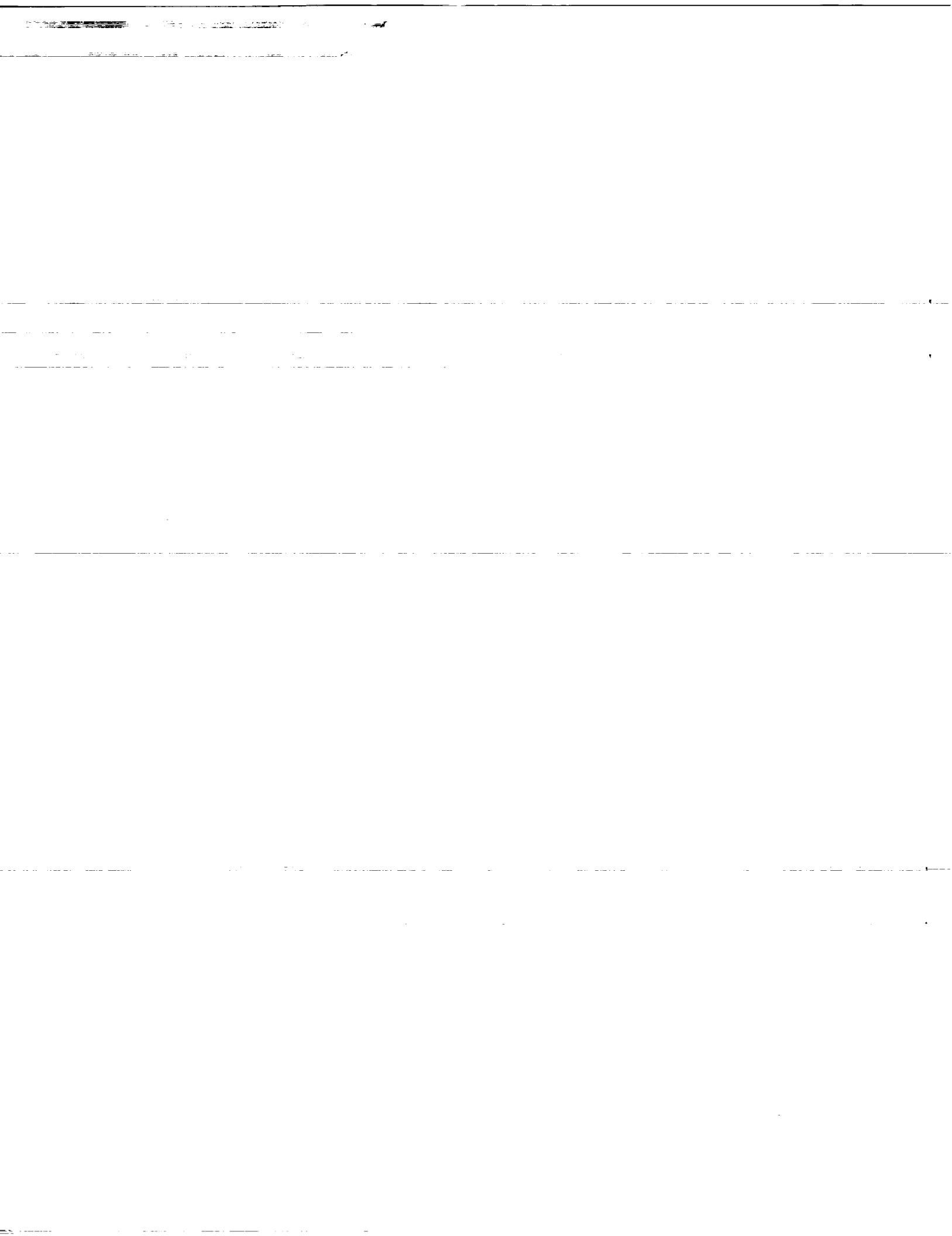
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PROMISES AND CHALLENGES

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ABSTRACT

Pitch based graphitized carbon fibers with electrical resistivity of 300  $\mu\Omega$ -cm were brominated and partially debrominated to 18 percent bromine at room temperature, and then fluorinated at 300 to 450 °C, either continuously or intermittently for several cycles. In addition, one fluorine and titanium fluoride intercalated fiber sample was fluorinated at 270 °C from the same fiber source. The mass and conductivity of the brominated-debrominated then fluorinated fibers (with fluorine-to-carbon atom ratio of 0.54 or higher) stabilized at room temperature air in a few days. However, at 200 °C air, these values decreased rapidly and then more slowly, throughout a 2-week test period. The electrically insulative or semiconductive fibers were found to be compatible with epoxy and have the fluorine-to-carbon atom ratio of 0.65 to 0.68, thermal conductivity of 5 to 24 W/m-K, electrical resistivity of  $10^4$  to  $10^{11}$   $\Omega$ -cm, tensile strength of 70 to 150 ksi, Young's modulus of 20 to 30 msi, and CTE values of 7 ppm/°C. Data of these physical property values are preliminary. However, it is concluded that these physical properties can be tailor-made. They depend largely on the fluorine content of the final products and the intercalant in the fibers before fluorination, and, to a smaller extent, on the fluorination temperature histogram.

## INTRODUCTION

Graphite materials are electrically conductive. Graphite reacts with fluorine between 400 and 460 °C to form an electrically insulating, chemically inert, hydrophobic, white material known as graphite fluoride  $(CF)_n$  (Ref. 1). In addition, fluorine and metal fluoride intercalated graphite react with fluorine gas at 250 °C or higher to form graphite fluoride. The resulting products have fluorine-to-carbon atom ratios between 0.5 and 1.0, and are believed to be a mixture of  $(CF)_n$  and  $(C_2F)_n$  (Ref. 2). These products are commercially available in powder form and are primarily used as dry lubricants or cathode materials in lithium batteries.

In a recent study, pitch based graphitized carbon fibers, exposed to saturated bromine vapor and debrominated in room temperature air, were found to react with fluorine in 275 to 450 °C temperature range. This treatment produced fibers stronger and more thermally conductive than those using pristine graphite fiber as the starting material for fluorination (Ref. 3). Pristine graphitized carbon fibers were found to be either nonreactive to fluorine at low temperature, or too reactive to fluorine at high temperature. Therefore the products, if fluorinated, had severely damaged structure and therefore low thermal conductivity (Ref 3). No intermediate temperature range was available to producing high electrical resistivity and high thermal conductivity fibers made from pristine graphitized carbon fibers.

The thermal conductivity of the brominated-debrominated, then fluorinated fibers was measured to be 5 W/m-K or five times the fiberglass value, while its resistivity was measured to be larger than  $10^{11}$   $\Omega$ -cm. Composites made from this fluorinated fibrous insulator have high thermal conductivity, thus inviting their use to dissipate waste heat generated in power generation systems, such as printed circuit boards.

In order to be a good engineering material, the thermally conductive and electrically insulative fiber described above needs to be compatible with the surrounding materials and environment. Therefore, modulus and tensile strength, room temperature and high temperature stability, coefficient of thermal expansion, and wetting behavior of the fibers with epoxy were measured. The possibility of producing graphite fluoride fibers with tailor-made physical properties for specific applications was also explored.

#### EXPERIMENTAL METHODS

The first set of fibers discussed in this report is graphitized pitch based carbon fibers Amoco P-100 (interplanar spacing 3.37Å) brominated at room temperature with bromine vapor, partially debrominated at room temperature air and stabilized to a bromine content of 18 percent by weight, and then fluorinated at 300, 350, 370, 390, and 450 °C for 21 hr. The P-100 fiber was used as the starting material because brominated P-100 was the best understood of the brominated fibers (Ref. 4).

The second set of fibers discussed in this report is Amoco P-100 fibers, brominated and partially debrominated at room temperature air, and then fluorinated intermittently at 350 or 370 °C for several cycles. In every cycle, the fibers were fluorinated for 10.5 hr followed by nitrogen heating for 3.5 hr. The purpose of these experiments was to determine the effect of the fluorination temperature histogram on the physical properties of the fluorinated products.

An additional P-100 fiber sample was intercalated with fluorine and titanium foil at 190 °C for 31 hr and then fluorinated at 270 °C for 21 hr (Ref. 5). In this experiment titanium fluoride intercalated fiber was the starting material for fluorination. The purpose of this experiment was to

find the effect of intercalants in the fibers on the physical properties of the fluorinated products.

Electrical resistance, and therefore the electrical resistivity values of the graphite fluoride fiber products described above were obtained using the conventional two-point method. Resistance of single filaments (10 to 15  $\mu\text{m}$  diam) was measured whenever possible. Resistance of fiber strands of 2000 filaments was measured whenever the single filament's resistance was too high to be measured by the available instruments.

The tensile strength and modulus of these fibers were measured using a method modified from the bending method proposed by Sinclair (Ref. 6). From his work, the following two equations were obtained:

$$E = E_o \left( \frac{T}{T_o} \right) \left( \frac{D}{D} \right)^2 \left( \frac{d_o}{d} \right)^4$$
$$\sigma = E \frac{d}{D_b}$$

where  $E$  is the fiber modulus,  $\sigma$  is the tensile strength,  $T$  is the tension of the entire bending fiber,  $D$  is the minimum diameter of curvature of the entire fiber, and  $d$  is the fiber diameter. The subscript  $o$  indicates that the values are for a fiber with known modulus. The subscript  $b$  indicates that the bending fiber is at the breaking point. During the experiments for modulus estimation, one end of the fiber was bent against the platform of an electronic balance which measured to 0.1 mg. The other end of the fiber was against an external force to form a 180 degree loop. The minimum diameter of curvature of the fiber was controlled to be constant for all samples throughout the experiment. From mechanics theory, the value  $T$  in the above equation is equal to the electronic balance readings obtained from the bending fiber. During the experiment for tensile strength, a 360 degree fiber loop was formed

by hand. By pulling one of the fiber ends, the loop diameter decreases continuously until broken. The minimum diameter of the fiber loop was measured by a ruler under a magnifying glass.

The standard fiber for modulus estimation was P-100, whose modulus was 105 msi. Using this method, the brominated P-100 was found to have modulus and tensile strength of 89 msi and 230 ksi, respectively. These are 9 and 21 percent less than the values obtained from the conventional method (98 msi and 291 ksi, respectively) (Ref. 7.).

The fiber fluorinated at 300 and 350 °C was tested for coefficient of thermal expansion (CTE). It was placed on a flat material with known CTE. One end of the fiber was fixed on the flat substrate by carbon paint. The other end was observed by a microscope and was allowed to move during heating or cooling by turning on or off a heating lamp. The direction and magnitude of such a move was observed by the microscope and used, along with the temperature increase of the substrate, the fiber length, and the CTE of the background material, to calculate the CTE of the fiber. This method assumes that the fibers extend or shrink freely on the background material. However, the fiber actually adheres to the background material to some extent, causing the calculated value be the maximum possible CTE if the substrate material expands faster than the fiber during heating, and minimum possible CTE if otherwise. Using soda lime glass slide (CTE: 9 ppm/°C) and P-100 epoxy composite (CTE: -1 ppm/°C) as substrate materials, a range of CTE for the fiber fluorinated at 350 °C was obtained. Using molybdenum plate (CTE: 5 ppm/°C) as substrate material, the maximum possible CTE for fiber fluorinated at 300 °C was obtained.

The thermal stability of the fibers described above was evaluated by placing them in air at 200 °C and measuring the electrical resistances of individual filaments for 2 weeks.

X-ray diffraction data of a few typical fluorinated fiber samples described in this report were taken to study its molecular structure.

A scanning electron microscope was used to take both EDS data and secondary electron micrographs. Using the micrographs, structural damage at both the side surfaces and the ends of the graphite fluoride fibers were examined. Also, knowing the bromine content in the fiber was 18 percent of carbon mass (Ref. 4) before fluorination, EDS data and weight changes during fluorination of these fibers were used to estimate their fluorine and bromine contents.

The wetting between the fluorinated fiber and epoxy was examined by putting a small drop of epoxy on a fiber filament and observing the wetting behavior under an optical microscope.

The physical property data obtained from the method described above are preliminary. However, they served the purpose of determining if the physical properties of the fluorinated graphitized carbon fiber can be tailor-made. Also, they serve the purpose to determine if the fibers can be compatible with the environment.

## RESULTS AND DISCUSSION

Table 1 summarizes the fluorine and bromine content, electrical resistivity, thermal stability at 200 °C, mechanical properties, thermal expansion coefficient, and epoxy-wetting data of the graphite fluoride fibers obtained from the experiments described in this report.

Comparing continuous fluorination to cycles of fluorination and nitrogen heating, Table 1 shows that if the total fluorination time and fluorination



temperature were the same, the latter resulted in higher fluorine content products than the former did. This can be explained by proposing that, during the nitrogen heating period, the structure of the partially fluorinated fiber was rearranged to facilitate further fluorination in the subsequent fluorination period.

In room temperature air, the electrical resistivity values of newly fluorinated fibers decreased and stabilized in a few days. The stabilized electrical resistivity values are listed in Table 1. Several phenomena were observed when measuring the electrical resistivity:

(1) For some graphite fluoride fibers with fluorine-to-carbon atom ratio in the 0.54 to 0.65 range, the resistivity decreased by as many as three order of magnitudes while the weight decreased by only 0.4 percent during the ambient condition stabilization. One reason that can be used to explain this phenomenon is that the fibers at the fluorine content described above contained electrically conductive regions which were isolated by thin electrically insulative barriers. Therefore, a small disturbance of these fibers destroyed some of the insulative barrier, resulting in the free flow electrons and therefore low electrical resistivity.

(2) When measuring the electrical resistivity of a 4-cm-long  $\text{CF}_{0.65}$  fiber sample, the value was  $3.6 \times 10^4 \Omega\text{-cm}$  when the voltage across the sample was 10 V. This resistivity value dropped to  $5.2 \Omega\text{-cm}$  when the voltage across the fiber was raised to 20 V. The new resistivity value remained unchanged even after the voltage across the sample was again reduced to 10 V. This phenomenon was not observed for samples with a fluorine-to-carbon atom ratio larger than 0.65. The proposed electronic structure described in the last paragraph can again be used to explain this phenomenon. For this particular sample, x-ray data, which

contain the peaks for the conductive graphite and the insulative graphite fluoride, support the proposed electronic structure (Fig. 1).

Figure 2 was obtained from the tensile strength and resistivity data in Table 1. This figure shows that fibers produced from two cycles of fluorine reaction followed by nitrogen heating (black circle data points) were slightly stronger and/or more electrically resistive than those produced from one continuous fluorine heating (open circle data points connected by solid line). But, fibers produced from five cycles of fluorine reaction followed by nitrogen heating (black triangle data points) are slightly weaker and/or less electrically resistive than those produced from one continuous fluorine heating. Such a difference may be real, but it is too small to make a definite conclusion concerning the effect of fluorination temperature histogram on the fluorinated product quality.

Figure 2 also shows that the graphite fluoride produced from titanium fluoride intercalated fibers (black square point) becomes very fragile (low tensile strength) before its electrical resistivity reaches semiconducting range. Therefore, for the process described above, bromine is a better intercalant than titanium fluoride to produce strong and electrically insulative graphite fluoride fibers.

Further study is needed to improve the fluorinated product quality by using proper fluorination temperature histograms and proper intercalants.

Figure 3 shows the electrical resistivity, the Young's modulus and the tensile strength as functions of the fluorine content in the graphite fluoride fibers produced from brominated P-100 fibers. The fibers are electrically conducting when the fluorine-to-carbon atom ratio is  $<0.6$ , semiconducting when it is  $0.6$  to  $0.68$ , and insulating when it is  $\geq 0.68$ . The electrical resistivity of the fibers increases sharply when the fluorine content is in the  $0.55$  to

0.68 range. It eventually becomes an insulator when the fluorine content reaches 0.68. These data suggest the possibility that, after removing all conducting electrons by fluorination, one has a stable intermediate product,  $C_3F_2$ . This suggestion is supported by the observation that fluorine content of 0.68 can be obtained with 350 and 370 °C fluorination temperature, but fluorine content higher than 0.68 cannot be obtained unless fluorination temperature was raised to 390 °C or higher, where the fluorine starts to react with the pristine P-100 fibers (Ref. 3).

Young's modulus of fluorinated fibers decreases smoothly from 100 to 10 msi with fluorine content increasing from 0 to 0.76, but the tensile strength starts to decrease sharply only when the fluorine content reaches the 0.5 to 0.6 range. When the fluorine content is low, the tensile strength decreases slightly with increasing fluorine content if it is expressed in force per unit area. However, since the fiber diameter increases during fluorination, this value remains practically unchanged if it is expressed in force per individual fiber.

At 30 °C, the coefficient of thermal expansion for fibers  $CF_{0.074}Br_{0.021}$  was estimated to have a maximum value of -2 ppm/°C. Since the CTE of this fiber is believed to be equal to, or larger than the CTE of pristine graphite fibers (-1.6 ppm/°C), the CTE of this fiber is believed to be equal to its estimated maximum possible value, or -2 ppm/°C.

Also at 30 °C, the coefficient of thermal expansion for fibers with  $CF_{0.61}$  was estimated to be in the 6 to 8 ppm/°C range. Using this value and Young's modulus data shown in Table 1, the theoretical CTE for 40 percent fill composite made from this fiber and epoxy was calculated to be 7 to 9 ppm/°C (Ref. 8). Therefore, printed circuit boards made from this composite appear to be CTE compatible with silicon (3 to 7 ppm/°C CTE value).

The electrical resistivity of the graphite fluoride fibers changed rapidly during the first several hours of heating at 200 °C. The rate of resistivity change then slowed down gradually, but did not stop throughout the heating period. However, when the fibers were removed from the heating environment and placed in room temperature air at any time, the resistivity stopped changing and was found to remain constant for a month afterward.

At 200 °C, the fibers become significantly less conductive if the fluorine content is 7 percent, but much more conductive if the fluorine content is 54 percent or higher. This may be a result of the small amount of fluorine loss, or a structural rearrangement in the fiber during heating, or both.

It is thus concluded that the graphite fluoride fibers described in this report was not stable at 200 °C air. However, other researchers have previously reported graphite fluoride to be thermally stable up to near 400 °C (Ref. 1). Such difference may be due to the fiber structural damages which occurred during and after fluorination reaction described in this report. The structural damages created active sites, and therefore resulted in oxidation in the fibers during heating in air at 200 to 400 °C.

It is also possible that the graphite fluoride described in this report had  $sp^2$  electron configuration for the carbon atom, while the graphite fluoride in the previous report had  $sp^3$  electron configuration for the carbon atom (Ref. 9).

For the purpose of understanding why the thermal stability of the graphite fluoride fibers described in this report is lower than that of the graphite fluoride described by other researchers previously, additional research was conducted and will be published (Ref. 10).

Figure 4 is x-ray data for a typical graphite fluoride fiber sample. This fiber sample, also described in Table 1, was brominated P-100 exposed to five

cycles of 350 °C, 10 hr fluorine followed by 350 °C, 5 hr nitrogen. Its fluorine-to-carbon atom ratio, electrical resistivity and thermal conductivity were 0.65,  $3 \times 10^6$   $\Omega$ -cm and 24 w/m-K, respectively. This x-ray data are similar to those taken from a C<sub>2</sub>F sample described by Touhara et al., having broad peaks at 8 to 11° and 40 to 45° ranges (Ref. 11). These correspond to interplanar spacings of approximately 8 to 9 Å and 2 to 2.4 Å, respectively.

Energy dispersive spectroscopy data was used to estimate the amount of bromine in the graphite fluoride fibers. Contrary to previous reports (Ref. 3), these data indicates that most bromine leaves the samples during the fluorination process. Figures 5(a) and (b) are the EDS spectrums of the side surface and the end tip, respectively, of a single CF<sub>0.76</sub> fiber described in Table 1. No bromine peak at 1.6 keV can be observed. Figure 5(c) is the EDS spectrum of the end tip of a CF<sub>0.60</sub> fiber sample. It contains a bromine peak. The bromine peak is much smaller than that in Fig. 5(d), which displays the spectrum of the end tip of a typical fiber containing 18 percent bromine.

It is noted from the above described EDS data that the end tip of the CF<sub>0.76</sub> filament has lower fluorine-to-carbon ratio than either its side surface or the end tip of the CF<sub>0.60</sub> filament. It is suggested that the structural damage at the end tip of the CF<sub>0.76</sub> is severe, resulting in fluorine loss.

Figure 6 shows SEM micrographs taken from the ends of some typical graphite fluoride fibers. Structural damage at the ends of all graphite fluoride fibers can be observed. Structural damage on the side surfaces of all graphite fluoride can also be found. This damage is shown in the micrographs in Fig. 7.

The above described SEM micrographs suggest that the fluorinated fibers have structural damages parallel to their lengths, and therefore may have low transverse tensile strength.

Figure 8 shows the wetting behavior between epoxy and both graphite and graphite fluoride fibers on glass slides. All fibers observed in this experiment were found to have near zero degree contact angle with epoxy. This suggests that epoxy can be used to fabricate fluorinated graphite composites because the epoxy wets the fibers. A graphite fluoride epoxy composite (2.5 by 2.5 by 0.5 cm) made from the graphite fluoride fabric  $CF_{0.61}$  and described in Table 1 and Fig. 8 was fabricated. It appears to be strong enough to withstand regular handling. Further work is needed to fabricate and characterize the graphite fluoride-epoxy composites.

#### CONCLUSIONS

Using the method described in this report, graphite fluoride fibers can have resistivity near  $10^{11} \Omega\text{-cm}$ , thermal conductivity  $\geq 5 \text{ W/m-K}$  (five times that of fiberglass), tensile strength near 80 ksi, and Young's modulus near 25 msi. Or, for a more thermally conductive product with electrical resistivity in semiconductive range, the fibers can be fabricated such that these properties have the values  $3 \times 10^6 \Omega\text{-cm}$ ,  $24 \text{ W/m-K}$ , 80 ksi, and 24 msi, respectively. Coefficient of thermal expansion (CTE) of the  $CF_{0.074}Br_{0.021}$  and the  $CF_{0.61}$  samples were estimated to be -2 and 7 ppm/ $^{\circ}\text{C}$ , respectively. Scanning electron micrographs indicate that the fluorinated fibers have structural damages parallel to their lengths, and therefore may have low transverse tensile strength.

Instead of continuous fluorination, cycles of fluorination followed by nitrogen heating results in the reduction of total fluorination time and/or temperature. However, the effects of temperature histogram on the final product quality is inconclusive at this time.

As an intercalant, titanium fluoride was found to produce weaker and lower resistivity fibers than bromine, indicating that the type of intercalant in the fiber can effect the quality of the fluorinated product.

The fibers produced in this lab were stable at room temperature air, but unstable at 200 °C. Previously, graphite fluoride fibers produced by other researchers were found stable at 400 °C. The reason for such a discrepancy may be related to the fiber structural damage that occurred during and after fluorination. Additional research on the thermal stability of graphite fluoride was conducted and will be published. In future work, reducing the fiber structural damage by using new types of fibers, new intercalants, and new fluorination temperature histograms will be examined. This work is expected to result in fibers with improved thermal stability, thermal conductivity, and longitudinal and transverse tensile strength.

As the fluorine-to-carbon atom ratio increases from 0 to 0.68, the modulus decreases from 90 to 20 msi, and the thermal expansion coefficient increases from -2 to 6 to 8 ppm/°C. It appears that by properly controlling the fluorine content in the fiber, its modulus and coefficient of thermal expansion, as well as electrical resistivity, can be tailor-made.

The graphite fluoride fiber can wet epoxy, with the contact angle near 0°. Therefore epoxy can be used with the graphite fluoride fibers to form a composite as an engineering material whose physical properties, similar to those of the graphite fluoride described above, can be tailor-made.

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#### REFERENCES

1. W. Rudoff, Inorg. Chem. and Radiochem., 1, 223 (1959).
2. N. Watanabe, T. Nakajima, and M. Kawaguchi, U.S. Patent No. 4,423,261.
3. C. Hung, M. Long, and M. Stahl, SAMPE Q., 19, 12 (1988).
4. D. Jaworski, J. Gaier, C. Hung, and B. Banks, SAMPE Q., 18, 9 (1986).
5. T. Nakajima, K. Nakane, M. Kawaguchi, and N. Watanabe, Carbon, 25, 685 (1987).
6. D. Sinclair, J. Appl. Phys., 21, 380 (1950).
7. K.J. Chen, and R.J. Diefendorf, Personal communication (1985, 1988).
8. Polymer Engineering Composites (Edited by M.O.W. Richardson) Applied Science Publishers, LTD, London (1977).
9. N. Bartlett, Department of Chemistry, University of California, Berkeley, Personal Communication (1989).
10. C. Hung, unpublished research.
11. H. Touhara, K. Kadono, Y. Fujii, and N. Watanabe, Z. Anorg. Allg. Chem., 544, 7 (1987).



TABLE 1. - PHYSICAL PROPERTIES OF FLUORINATED P-100 FIBERS

Reaction temperature, °C	Fluorination time per cycle, hr	Nitrogen heating time per cycle, hr	Number of cycles	Fluorine-to-carbon atom ratio	Bromine-to-carbon weight ratio	Resistivity before heating, $\Omega$ -cm	Resistivity ratio of 200 °C treated to nonheated fibers	Tensile strength, ksi	Modulus, msi	Thermal expansion coefficient, ppm/K	Contact angles with epoxy, deg
---	---	---	---	0	0	$2.5 \times 10^{-4}$	1.0	325	105	-1.6	~0
300	21	0	1	.074	.18	$5.0 \times 10^{-5}$	1.0	230	89	---	↓
350	↓	↓	↓	.54	.14	$1.2 \times 10^{-4}$	1.3	240	84	-2	---
a350	↓	↓	↓	.61	.03	$2.0 \times 10^{-2}$	0.2 to 0.7	206	50	---	---
370	↓	↓	↓	.67	.025	$3.0 \times 10^2$	---	158	32	6 to 8	---
390	↓	↓	↓	.71	.018	$2.0 \times 10^9$	---	119	33	---	---
450	↓	↓	↓	.76	.01	$1.0 \times 10^{12}$	---	74	20	---	---
350	10.5	3.5	2	.65	0	$b > 10^1$	(b)	35	11	---	~0
370	10.5	3.5	2	.68	.01	$d4.0 \times 10^4$	---	150	30	---	---
350	10	5	5	.68	.01	$5.0 \times 10^{10}$	---	123	33	---	---
a350	10	5	5	.65	.01	$8.0 \times 10^6$	---	79	23	---	---
					.01	$3.0 \times 10^6$	0.025	89	24	---	---
(Fluorination of titanium fluoride intercalated fiber) <sup>c</sup>				(95 percent weight increase)		1.76	---	56	23	---	---

<sup>a</sup>These two runs used a different P-100 source as starting material.

<sup>b</sup>Resistivity of this fiber was too high to be measured in this lab.

<sup>c</sup>P-100 fibers were first placed in a fluorine environment in the presence of titanium foil at 190 °C for 31 hr, then placed in 270 °C fluorine for 21 hr.

<sup>d</sup>A small fraction of the fibers (2 out of 14 filaments) have very low resistivity ( $\sim 10^{-3} \Omega$ -cm) and are excluded from this data point.

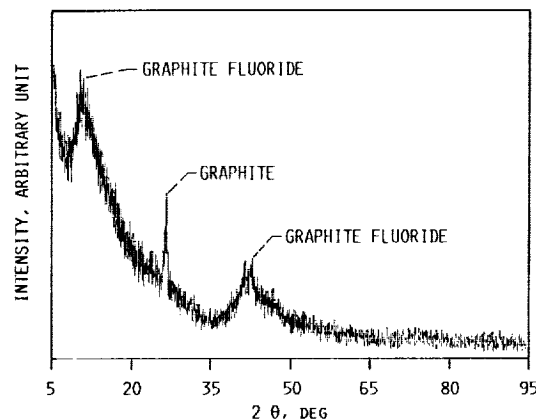


FIGURE 1. - X-RAY DIFFRACTION DATA FOR THE  $CF_{0.65}$  FIBERS OBTAINED FROM TWO CYCLES OF 10.5 HOURS OF FLUORINATION AT  $350^\circ C$  FOLLOWED BY 3.5 HOURS OF NITROGEN HEATING AT  $350^\circ C$ .

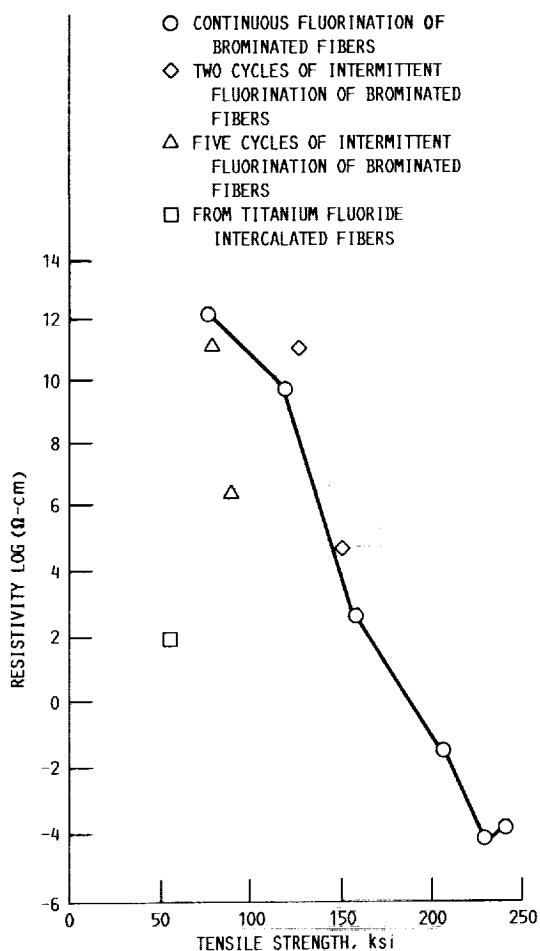


FIGURE 2. - ELECTRICAL RESISTIVITY VERSUS TENSILE STRENGTH PLOT FOR GRAPHITE FLUORIDE FIBERS.

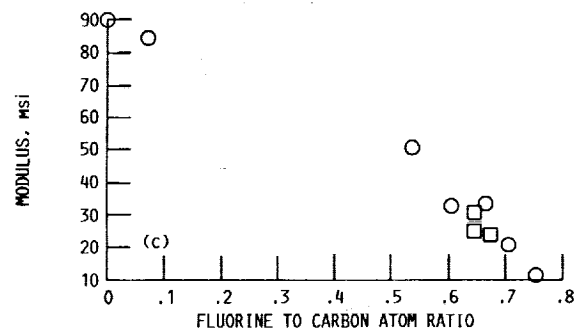
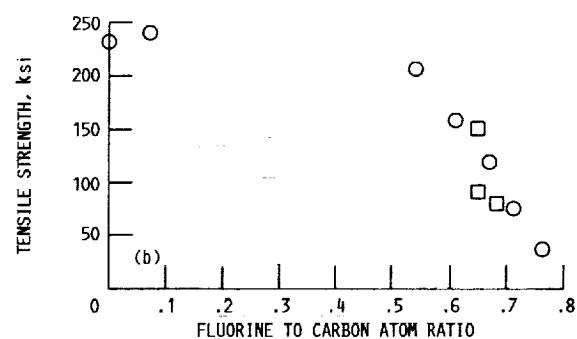
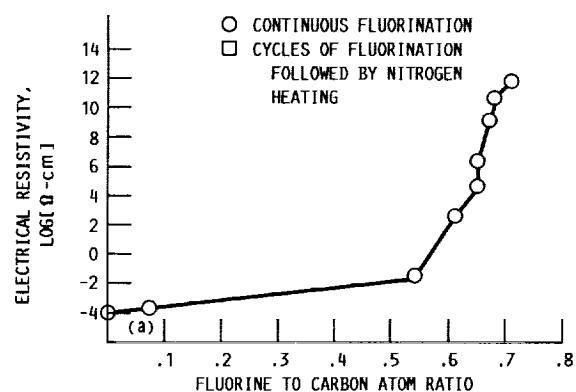


FIGURE 3. - ELECTRICAL RESISTIVITY AND MECHANICAL PROPERTIES AS FUNCTIONS OF FLUORINE CONTENT.

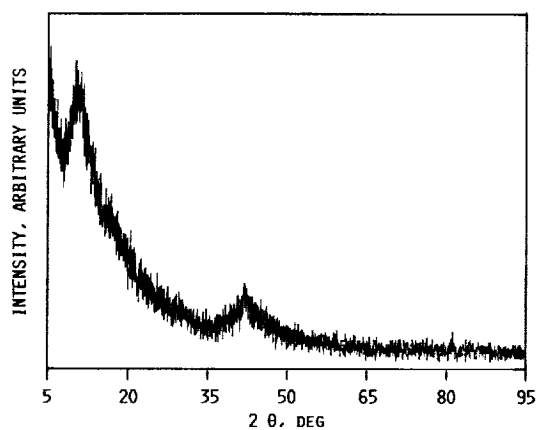


FIGURE 4. - X-RAY DIFFRACTION DATA FOR THE GRAPHITE FLUORIDE FIBERS  $CF_{0.65}$  PRODUCED BY FIVE CYCLES OF 10 HOURS OF FLUORINATION AT  $350^{\circ}C$  FOLLOWED BY 5 HOURS OF NITROGEN HEATING AT  $350^{\circ}C$ .

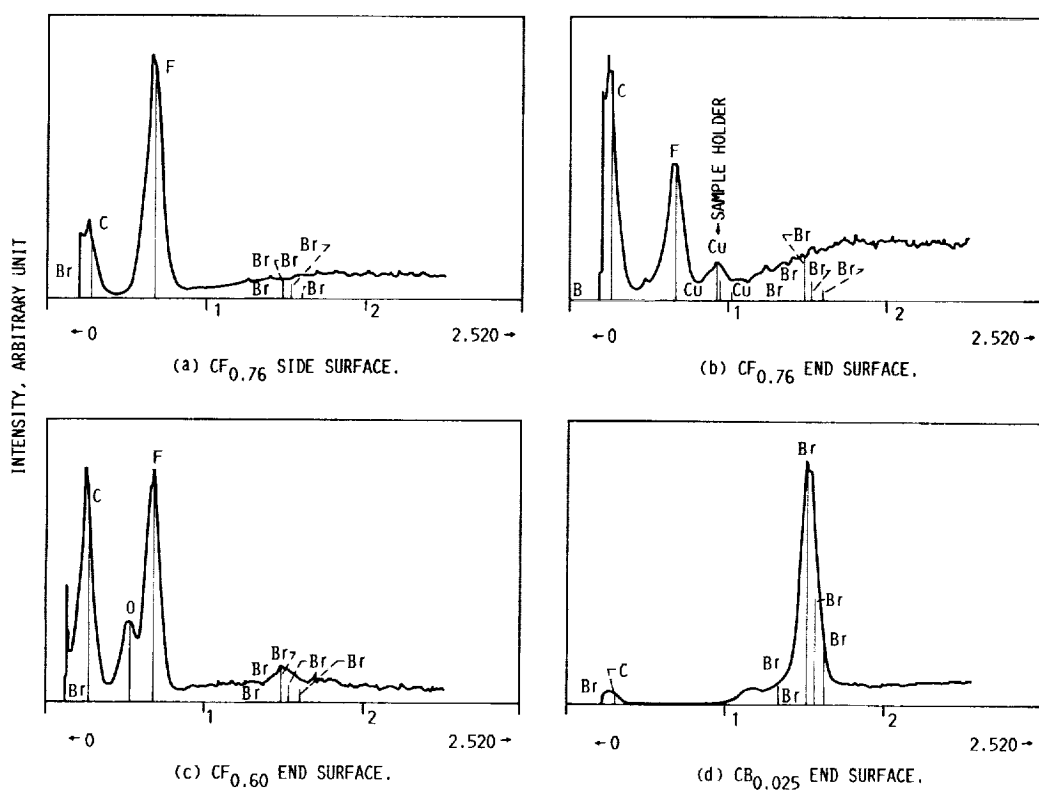
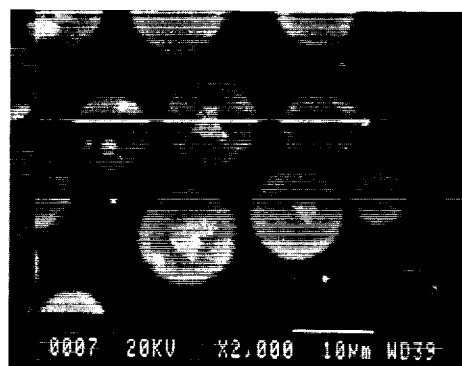
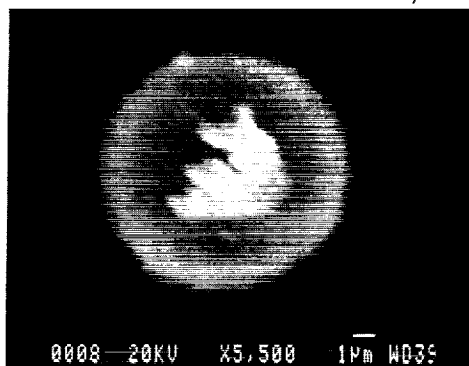
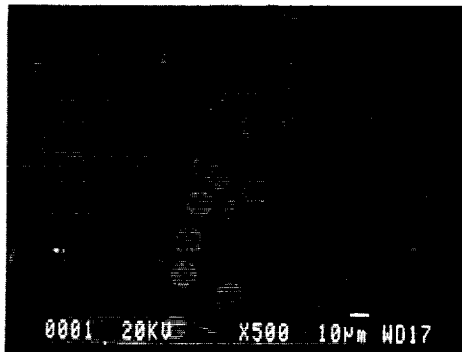
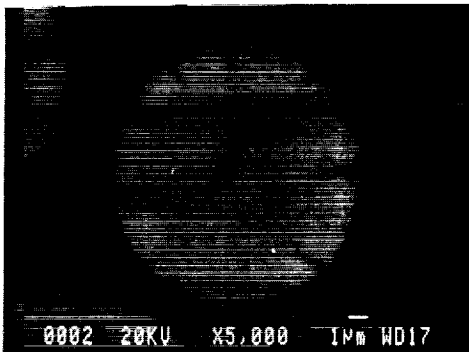


FIGURE 5. - ENERGY DISPERSE SPECTRUM (EDS) FOR GRAPHITE FLUORIDE FIBERS.

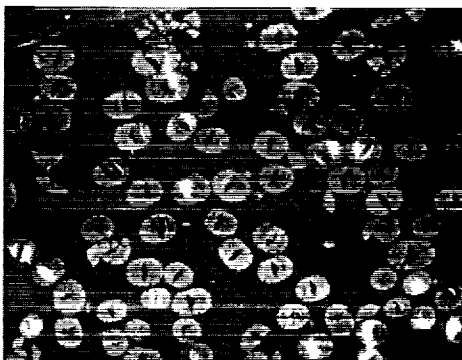
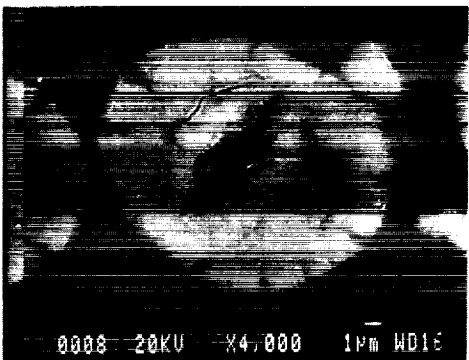
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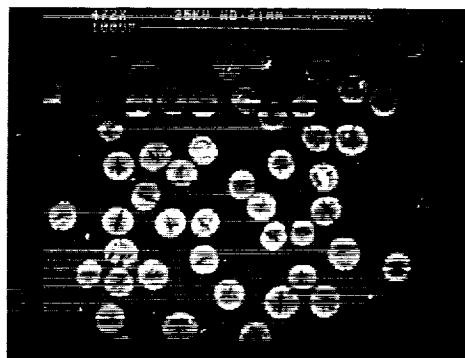
(a)  $\text{CF}_{0.074}\text{Br}_{0.020}$



(b)  $\text{CF}_{0.60}$



(c)  $\text{CF}_{0.76}$



(d)  $\text{CF}_{0.65}$

FIGURE 6. - STRUCTURAL DAMAGE AT THE END SURFACES OF THE GRAPHITE FLUORIDE FIBERS.

ORIGINAL PAGE  
BLACK AND WHITE PHOTOGRAPH

ORIGINAL PAGE IS  
OF POOR QUALITY



(a) CF<sub>0.65</sub>



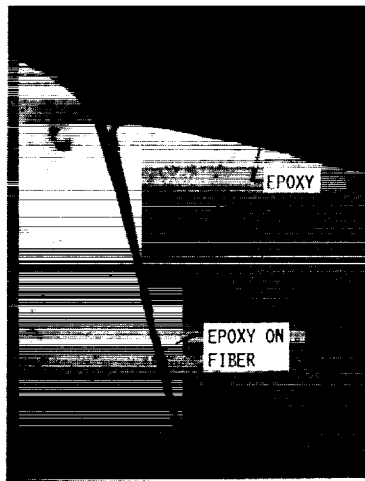
(b) CF<sub>0.61</sub>



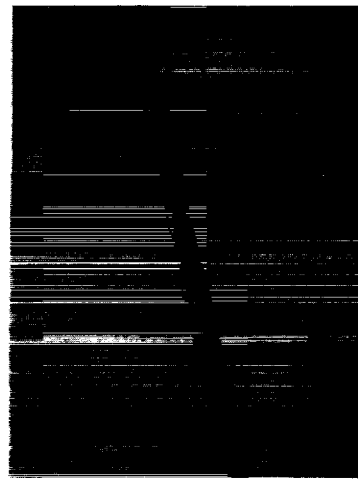
(c) CF<sub>0.67</sub>

FIGURE 7. - STRUCTURAL DAMAGE AT THE SIDE SURFACES OF THE GRAPHITE FLUORIDE FIBERS.

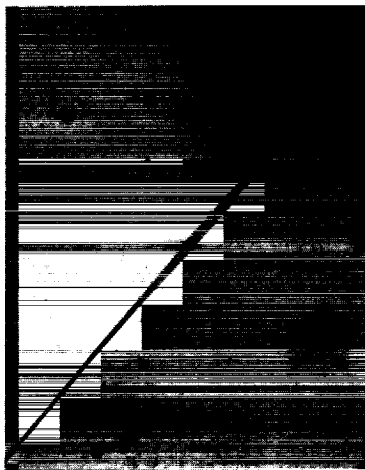
ORIGINAL PAGE  
BLACK AND WHITE PHOTOGRAPH



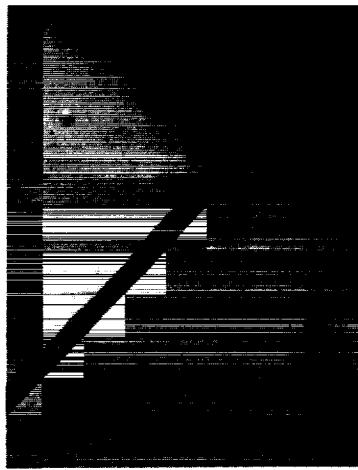
(a)  $CB_{0.025}$



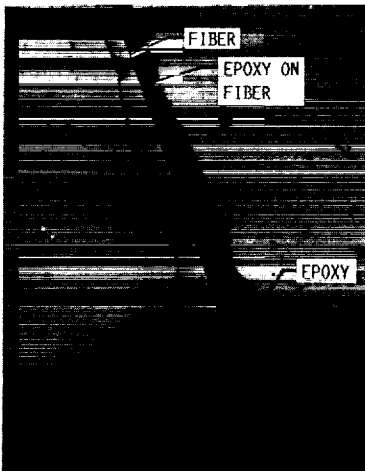
(A)  $CB_{0.025}$



(b)  $CF_{0.61}$

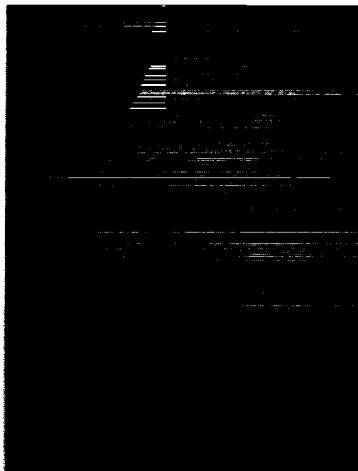


(B)  $CF_{0.61}$



(c)  $CF_{0.76}$

BEFORE CURING



(c)  $CF_{0.76}$

AFTER CURING

FIGURE 8. WETTING BEHAVIOR BETWEEN GRAPHITE FLUORIDE FIBERS AND EPOXY.



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16. Abstract Pitch based graphitized carbon fibers with electrical resistivity of $300 \mu\Omega\text{-cm}$ were brominated and partially debrominated to 18 percent bromine at room temperature, and then fluorinated at 300 to 450 °C, either continuously or intermittently for several cycles. In addition, one fluorine and titanium fluoride intercalated fiber sample was fluorinated at 270 °C from the same fiber source. The mass and conductivity of the brominated-debrominated then fluorinated fibers (with fluorine-to-carbon atom ratio of 0.54 or higher) stabilized at room temperature air in a few days. However, at 200 °C air, these values decreased rapidly and then more slowly, throughout a 2-week test period. The electrically insulative or semiconductive fibers were found to be compatible with epoxy and have the fluorine-to-carbon atom ratio of 0.65 to 0.68, thermal conductivity of 5 to 24 W/m-K, electrical resistivity of $10^4$ to $10^{11} \Omega\text{-cm}$ , tensile strength of 70 to 150 ksi, Young's modulus of 20 to 30 msi, and CTE values of 7 ppm/°C. Data of these physical property values are preliminary. However, it is concluded that these physical properties can be tailor-made. They depend largely on the fluorine content of the final products and the intercalant in the fibers before fluorination, and, to a smaller extent, on the fluorination temperature histogram. <i>ppm/deg C</i> <i>(coefficient of thermal expansion)</i>					
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